学校编码：**10384** 密级_____

学号：**22420111151401**

硕 士 学 位 论 文

南海北部甲烷水合物潜在区沉积物早期成岩过程中的碳硫相互作用

The coupling of carbon and sulfur in sediments in the early diagenesis of methane hydrate potential area of northern South China Sea

张劼

指 导 教 师： 雷怀彦 教授

专 业 名 称： 海 洋 地 质

论文提交日期: **2014** 年 **5** 月

论文答辩日期: **2014** 年 **5** 月

学位授予时间 **2014** 年 月

2014 年 5 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下，独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（　　）课题（组）的研究成果，获得（　　）课题（组）经费或实验室的资助，在（　　）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

目录

Contents

缩略语表

ANME Methanotrophic archaea 噬甲烷古菌

AOM Anaerobic oxidation of methane 甲烷厌氧氧化作用

AOM-SR Anaerobic oxidation of methane-sulfate reduction 甲烷厌氧氧化-硫酸盐还原作用

AVS Acid volatile sulfide 酸可挥发性硫

BSR Bottom simulating reflector 似海底反射界面

EMS Electron microscope scanning 扫描电子显微镜

pH Power of hydrogen pH 值

PVC Polyvinyl chloride 聚氯乙烯

SCS South China Sea 南中国海

SMI Sulfate-methane interface 硫酸盐甲烷交接面

SMTZ Sulfate-methane transition zone 硫酸盐-甲烷过渡带

SR Sulfate reduction 硫酸盐还原作用

SRB Sulfate reducing bacteria 硫酸盐还原菌

TC Total carbon 总碳

TOC Total organic carbon 总有机碳

TS Total sulfate 总硫

摘要

天然气水合物作为21世纪理想的替代能源，成为了全球科学界的研究热点。天然气水合物在地层中能否稳定存在主要受温度、压力、自身结构以及成份组成的影响。海平面升降、底层水温变化、沉积速率的改变等自然环境的变化及海底滑坡、地震和火山爆发等地质灾害的发生都会引起天然气水合物的突发性分解释放。我国南海北部作为天然气水合物的潜在赋存区，在地质历史中也曾多次发生天然气水合物的分解释放。天然气水合物所分解释放的甲烷向上逸散，与沉积物中的硫酸盐发生氧化还原反应，甲烷厌氧氧化-硫酸盐还原反应（AOM-SR）是沉积物早期成岩过程中最重要的反应之一，其反应过程不仅受到沉积物中的有机质和向上逸散的甲烷等碳源的影响，沉积物孔隙水中的硫酸盐也对反应有一定的控制作用。因此开展对我国南海北部甲烷水合物潜在区沉积物中碳硫作用的研究，不仅可以了解天然气水合物成藏过程，还可以了解天然气水合物在突发条件下的分解释放机理，更重要的是对我国寻找和勘探开发天然气水合物藏具有重要的科学意义。本论文依托国家“973”计划子课题“南海北部天然气水合物成藏的气源条件研究”（项目编号：2009CB21951）、国家自然科学基金项目“南海北部海底沉积层硫酸盐-甲烷体系产消机制及其界面（SMI）特征研究”（项目编号：40976035）和“天然气水合物成藏体系中产甲烷与甲烷厌氧氧化作用生物标志物和分子生物学研究”（项目编号：41276046）等项目，对台西南海域钻获的973-4沉积物柱状样进行了地球化学特征测定、自生黄铁矿镜下观察以及沉积环境分析，并结合区域地质特征、南海北部其他甲烷水合物潜在区的孔隙水特征等相关资料进行综合分析研究，获得以下主要认识：

（1）南海北部台西南海域973-4柱的有机碳含量为0.39-1.26%，TS含量为0.2-0.7%，AVS在898cm深度激增至9315μmol/g，黄铁矿$\delta^{34}S$含量在17.9‰~-44.4‰之间。利用973-4柱的地球化学特征综合判断：973-4柱存在有机质缺氧氧化硫酸盐还原与甲烷厌氧氧化还原硫酸盐两种硫酸盐还原路径，对应深度分别为360-440cm、580-900cm。其中甲烷厌氧氧化硫酸盐还原带可分为上下两部，对应深度分别为580-700cm、700-900cm，上部以甲烷含量作为AOM反应的限制条件，下部则受到硫酸盐含量的限制。甲烷厌氧氧化硫酸盐还原带上下部的分界

以硫酸盐梯度的突变为标志，此外，黄铁矿 $\delta^{34}S$ 含量接近 0‰及黄铁矿晶型出现二次生长也可作为辅助判断指标。

（2）973-4 柱 SMI 界面深度为 900cm，结合碳同位素结果和测年资料综合分析，认为 973-4 柱较浅的 SMI 界面深度预示着台西南海域可能存在有天然气水合物藏。

（3）通过分析南海北部多个站位的硫酸盐浓度随深度的变化情况，总结出南海北部硫酸盐含量随深度的变化可分为：表层有机硫氧化带、有机质缺氧氧化硫酸盐还原带、中部过渡带及甲烷厌氧氧化硫酸盐还原带。表层有机硫氧化带的出现与沉积物中有机质的含量与类型、局部地质构造及洋流有关，这种现象的发生常常集中出现。中部过渡带的出现与否不但取决于上部有机质缺氧氧化硫酸盐还原作用，而且与下部向上渗漏的甲烷通量相关。

（4）SMI 界面的深浅常常与下部是否赋存甲烷水合物藏关系密切，影响南海北部甲烷水合物潜在区 SMI 界面深度计算结果的因素复杂多样，本文首次提出了干扰数据的过滤方法，计算了南海北部多个站位的 SMI 界面深度，获得了新的合理的 SMI 界面。

（5）973-4 柱中黄铁矿以其形成机制可划分为两种：充填于生物碎屑及沉积物颗粒间的 I 型充填和交代充填于生物壳体碎屑中的 II 型充填。宏观上，黄铁矿可分为管状、块状及莓球状三种。黄铁矿集合体上部多为管状，中部为块状，深部为莓球状，充填型黄铁矿各个层位均有分布。黄铁矿集合体形态取决于形成时期沉积物颗粒间空隙大小及生物碎屑类型。

（6）973-4 柱中黄铁矿单晶可见截角立方体、立方体、八面体、五角十二面体及立方体与五角十二面体形成的聚型。八面体作为黄铁矿存在的主要晶型分布于各个层位中，其它几种晶型出现在 700cm 深度的沉积物中，此深度恰为 SMTZ 上下部的分界线，多晶型的存在代表着局部微环境的改变，而这种改变是 AOM 反应限制条件的变化造成的。这种限制条件的变化，可能是由于下伏甲烷水合物的分解偶发且不稳定，使得局部甲烷通量变化较大，最终导致在 SMTZ 中 AOM 反应的限制因素在 SO_4^{2-} 与 CH_4 之间随时发生改变，这种改变进而影响到黄铁矿的形成环境及路径。

（7）研究区沉积物早期成岩过程中，沉积物有机质中有较高活性有机质首

先通过氧化有机质的途径还原硫酸盐。随着高活性有机质的消耗，沉积物埋藏深度的增加，有机质缺氧氧化硫酸盐还原的过程受到抑制，低活性有机质在产甲烷带被产甲烷菌利用，生成甲烷，并在合适的条件下形成甲烷水合物。由于甲烷水合物赋存条件的改变，其分解释放的甲烷向上逸散，又为甲烷厌氧氧化硫酸盐还原作用提供甲烷，从而完成了整个早期成岩过程中碳硫相互作用。

关键词：天然气水合物；碳硫相互作用；硫酸盐-甲烷交接面（SMI）；黄铁矿；酸可挥发性硫（AVS）

Abstract

As an ideal alternative energy in the 21st century, gas hydrate has become a research focus in the global science field. The existing of gas hydrate is mainly under the influence of temperature, pressure and composition. Not only the variations of sea level, deposition rate and the sea water temperature at the bottom, but also sundry geological hazards, such as underwater landslides and earthquake can lead to the decomposition and release of gas hydrates. Therefore, by studying in coupling of carbon and sulfate in the gas hydrate potential zone in northern South China Sea, the accumulation process and the decomposition and release mechanism of gas hydrates under a gusty condition. As a potential zone of gas hydrate, the northern South China Sea also experienced the methane decomposition and release in geological history. Methane will be released and go upwards, which, subsequently, join in the anaerobic oxidation of methane-sulfate-reduction. Anaerobic methane oxidation-sulfate reduction (AOM-SR) is one of the most important reactions in the early diagenetic process of sediments, which is affected by the pore water in sediments and the carbon sources, such as organic matter and the lifting methane.

Moreover, it claims a guiding significance in the gas hydrates exploitation in our country. This research is on the basis of the National Major Fundamental Research and Development Project “Basic study on gas hydrate accumulation laws and exploitation in the South China Sea” (No. 2009CB219501), the National Nature Science Fundation Project “Research on the sulfate-methane system prosumer mechanism and its interface (SMI) characteristics of the sediments in the northern South China Sea” (project number: 40976035), and “Research tics on biomarkers and molecular biology of methanogenesis and anaerobic oxidation of methane in gas hydrate system” (project number:41276046).We chose the core 973-4 from the Taixinan area as the object of this research, for instance, the determination of geochemical characteristics, the observation of authigenic pyrite via microscope, the recovering of sedimentary environment, etc. Combining with the relevant research

materials and data (e.g., the regional geological features, other potential areas of methane hydrate in the northern South China Sea and, etc.), the following consequences are an outline of this study:

(1) The concentration of organic carbon in the core 973-4 from the Taixinan area amounts to 0.39-1.26%, and the correspondingly data of TS stands at 0.2-0.7%. At the depth of 898cm, AVS surges to 9315μmol/g. Besides, the concentration of δ34S in pyrite fluctuates between 17.9‰ and -44.4‰. By the apparent geochemical characteristics of 973-4 column, a comprehensive judgment comes into being: in 973-4 column, there are two sulfate reduction reactions-the anoxygenous oxidation of organic matter at the depth of 360-440cm and AOM at the depth of 580-900cm. The zone of the anoxygenous oxidation of organic matter could be divided into the upper portion locating at 580-700cm and the lower portion locating at 700-900cm. The boundary of these two parts above indicated mainly by the mutation of sulfate gradient in pore water and the diverseness and second growth of pyrite crystal.

(2) In 973-4 column, the depth of SMI is 900cm. According to the carbon isotope and dating, the shallow SMI of 973-4 column may claim the existing of gas hydrate in Taixinan area.

(3) Through analyzing the variations, with depth, of sulfate concentration in multiple sections in the northern South China Sea, the conclusions is the shifty sulfate concentration, which goes with its depth, in the northern South China Sea could be separated into three following parts: the surface oxidation zone of organic sulfur, the zone of the anoxygenous oxidation of organic matter, the central transitional zone and the zone of AOM. The surface oxidation zone of organic sulfur existing or not hinges on, frequently, three cases: the concentrations and types of organic matter in the sediments, regional geological structure and the influence of ocean current. Generally, the three cases above present all together. Correspondingly, the central transitional zone existing or not hinges on the anoxygenous oxidation of organic matter in the upper portion and the methane flux leaking upward in the lower portion.

(4) Generally, the depth of SMI has a close relationship with the existence of gas hydrates reserves in the lower portion. Multiple reasons contribute to the depth of SMI in gas hydrate potential area in the northern South China Sea. In this article, a filtering methodology for interferential data is put forward. By this methodology, the several depths of SMI in different sections have been recalculated in the northern South China Sea.

(5) The formation mechanisms of pyrite in 973-4 column can be partitioned into the type I filling and type II filling. The former type means filling among bioclastics and sediment particles, and metasomatically filling in bioclastics. At macro level, framboids pyrite. At macro level, pyrite has three categories, that is to say, framboids pyrite, tubular pyrite and massive pyrite. In terms of distribution in the aggregate forms of pyrite, tubular pyrite is a common existence in the upper portion, massive pyrite usually presents in the middle portion, and framboids pyrite shows in deeper portion relatively. Filling pyrite distributes all over every layer. Pyrite formation depends on bioclastics type and the collection period gap between sediment particle sizes. The aggregate forms of pyrite hinge on the types of bioclastics and the scales of the gap between sediments during formation.

(6) In 973-4 column, pyrite conveys multiple single crystals, for instance, cut corner cube, cube, octahedron, pentagonal dodecahedron and an aggregation consisting of cube and pentagonal dodecahedron. Thereinto, octahedron, acting as the main form of pyrite existences, spreads widely in every layer. By contrast, other crystals appear in the sediments at 700cm, which depth represents a boundary between the upper and lower portions of SMIZ. Various crystals indicate a shifty microenvironment, which attributes to various restrictive conditions of AOM. A possible inducement may be that the decomposition of methane hydrate, in the methane hydrate zone, is unstable and occasional, which due to a substantial fluctuation of methane flux. Consequently, the SO_4^{2-} and CH_4 in SMIZ as different restrictive conditions of AOM show an on-going fluctuation too, which, eventually, effects on the microenvironment and path of pyrite formation.

(7) The early diagenetic process of sediments in this study area, in the first place, the